Vacuum ultraviolet $4f^9 5d \to 4f^{10}$ interconfigurational transitions of Ho^{3+} ions in $LiLuF_4$ single crystals

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The laser-induced fluorescence spectrum (LIF) of $LiLuF_4$:Ho^{3+} single crystals pumped by a molecular F_2 pulsed-discharge laser at 157.6 nm is obtained in the vacuum ultraviolet (VUV) and UV regions of the spectrum. The observed transitions originate from the levels and the edge of the $4f^9 5d$ electronic configuration, and they are assigned to the $4f^9 5d \to 4f^{10}$ interconfigurational transitions. The LIF spectra for the dipole-allowed transitions can be explained provided that phonon trapping of the lattice vibrations is taking place within the Stark components of the $4f^9 5d$ electronic configuration. The absorption spectrum of the crystal samples in the VUV was obtained as well. We observed five main transitions between the ground level $^5I_8$ of the $4f^{10}$ electronic configuration and the Stark components of the levels of the $4f^9 5d$ electronic configuration in the spectral range between 125 and 150 nm, and we observed four main spin-forbidden transitions in the spectral range from 153 to 170 nm. © 1999 Optical Society of America [S0740-3224(99)00104-6]
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1. INTRODUCTION

Vacuum ultraviolet (VUV) and ultraviolet (UV) spectroscopy of rare-earth (RE) ions has become an important field of research recently because of the growing number of applications geared toward generating and detecting VUV radiation. The radiative interconfigurational $d–f$ transitions of the RE activated ions in the wide bandgap of dielectric crystals offer the possibility that these materials can be used for generating coherent VUV or UV light.[1] An optically pumped $LiYF_4$:Ce^{3+} crystal generated laser light at 325 nm,[2] and laser emission at 286 nm was obtained from a LaF_3:Ce^{3+} crystal.[3] Waynant and Klein[4] reported the first laser action in the VUV from solid-state dielectric crystals. They used a LaF_3:Nd^{3+} dielectric crystal to generate laser action at 172 nm when it was optically pumped by incoherent light[5] (emitted from excited Kr_2* molecules). Upconversion pumping arrangements with all solid-state laser elements[6,7] greatly simplify the experimental obstacles arising from VUV pumping. Fluorescent materials based on RE ions can also be used as high-quantum-efficiency phosphors[8] for plasma display screens and mercury-free light tubes,[9,10] for fast scintillators,[11] and for light-wave communications.[12] All of these applications are based on the intraconfigurational $4f^n \to 4f^n$ or the interconfigurational $4f^n \to 4f^{n-1}5d$ transitions of the trivalent RE ions. The $4f^n \to 4f^n$ transitions are parity forbidden. They are forced by the crystal field configuration mixing, and they appear to be weak and sharp. In contrast, the $4f^{n-1}5d \to 4f^n$ transitions are characterized by strong Frank–Condon factors, and their absorption and emission spectra are broadband owing to the high density of states of the $4f^{n-1}5d$ electronic configuration. In this paper

we report the interconfigurational $4f^9 5d \to 4f^{10}$ VUV and UV fluorescence and absorption features of Ho^{3+} ions in a $LiLuF_4$ single-crystal host as they are excited with the laser light from a F_2 pulsed-discharge molecular laser at 157.6 nm. This pumping arrangement has the advantage of populating the levels of the $4f^9 5d$ configuration directly from the ground level of the RE trivalent ion by means of only one-photon transitions. The subsequent deexcitation mechanism of the $4f^9 5d$ levels efficiently populates the levels of the $4f^{10}$ single configuration of the Ho^{3+} ions in a situation similar to the one described previously for other RE ions.[13] Some new fluorescence peaks were observed and assigned to the $4f^9 5d \to 4f^{10}$ electric dipole-allowed transitions of the Ho^{3+} ions.

The absorption spectra of the $LiLuF_4$:Ho^{3+} crystal samples were also recorded at room and liquid-nitrogen temperatures, for the first time to our knowledge, by use of a hydrogen lamp of stabilized longitudinal discharge. The absorption characteristics of the crystal samples in the VUV are due to the dipole-allowed transitions between the $^5I_8$ ground level of the RE trivalent ion and the Stark components of the levels of the $4f^9 5d$ electronic configuration. The numbers and the spacings of the components depend on the site symmetry of the RE ion and the intensity of the crystal field. We observed five main strong transitions between the $^5I_8$ ground level of the $4f^{10}$ electronic configuration and the Stark components of the levels of the $4f^9 5d$ electronic configuration of the Ho^{3+} ion in the spectral range between 125 and 150 nm. Four weak transitions were observed between the $^5I_8$ ground level of the $4f^{10}$ electronic configuration and the Stark components of the levels of the $4f^9 5d$ electronic configuration in the spectral range from 153 to 170 nm,

and they are attributed to spin-forbidden transitions between the ground level $^5I_8$ and the levels of the $4f^95d$ electronic configuration.

2. EXPERIMENT

The $LiLuF_4$:Ho^{3+} single crystals that were used for this study were grown by us from carbon crucibles by the Bridgman–Stockbarger method. The concentration of the RE ions in the samples varied from 1 to 0.1 at. %. The samples were optically polished disks or rods with 5-mm diameters, and their thicknesses varied between 0.5 and 2 mm. The experimental apparatus for obtaining the excitation spectrum was described previously.[13] It consists mainly of the laser pump source; the vacuum chamber with liquid-nitrogen cryogenic facility, where the crystal sample was placed; the focusing optics; and the detection electronics. The laser pump source was a molecular F_2 laser, which delivered 12 mJ of power per pulse. The pulse width at half-maximum was 12 ns. The laser beam was focused parallel to the optical axis of the crystal by a 60-cm concave aluminum mirror, coated with MgF_2, at a right angle to the laser axis. The fluorescent light was detected along the optical axis as well. A bandpass filter with 23% transmission at 157 and 26 nm bandwidths was placed in front of the crystal sample to reduce the scattered light from the laser discharge. The detection system consisted of a 0.2-m VUV monochromator (Acton VM 502), a solar-blind photomultiplier (EMI 9412) or a secondary electron multiplier (SEM), and a boxcar integrator, which was interfaced to a computer. The fluorescence spectrum was detected with a resolution better than 1 nm. The absorption spectrum in the VUV and UV was recorded with a hydrogen lamp constructed in our laboratory, operating in a longitudinal stabilized discharge mode. The high stability of the discharge and the processing of the optical signals provide a good signal-to-noise ratio (better than 2000). The optical paths of the pumping laser beam and of the fluorescence light signal were kept within stainless-steel vacuum lines at 10^{-6} mbar of pressure.

3. RESULTS AND DISCUSSION

A. Absorption Spectrum

The absorption spectrum of the trivalent Ho^{3+} ion was studied previously in a number of crystal lattices.[14–17] The electric crystal field splits all the levels of the single and the mixed configurations. Three Stark components of the levels of the $4f^95d$ electronic configuration were observed in the case of the BaY_2F_8 crystal host, with maximum absorption at 63 900 (156.4 nm), 67 800 (147.4 nm), and 71 800 cm^{-1} (139.2 nm). The edge of the levels of the $4f^95d$ electronic configuration[17] was at 63 125 cm^{-1} (158.4 nm). For the LaF_3 and the CaF_3 crystals the edges of the levels of the $4f^95d$ electronic configuration for dipole-allowed transitions were found to be at 63 300 (158.7 nm) and 64 100 cm^{-1} (156 nm), respectively.[14,16] In the free-ion case the edge of the levels of the $4f^95d$ electronic configuration was found[18] to be at 58 900 cm^{-1} (169.5 nm). In the case of the single $LiLuF_4$ crystal of the present experiment at room and liquid-nitrogen tempera-

tures, for 0.1 at. % concentration of Ho^{3+} ions, the edge of the levels of the $4f^95d$ electronic configuration was found to be at 65 789 cm^{-1} (152 nm) for those levels for which the $4f^{10} \rightarrow 4f^95d$ transitions appear to be strong (spectral range 125–150 nm). Apart from this, for those $4f^95d$ levels for which the $4f^{10} \rightarrow 4f^95d$ transitions appear to be weak, (spectral range 153–170 nm), the edge of the levels was found to be at 58 823 cm^{-1} (168 nm). The intensity of the absorption peaks in this spectral range increases with increasing concentration of the RE ion. For 0.1–1 at. % concentration of the RE ion, the absorption coefficient has its highest value at 156 nm. In the spectral range from 125 to 150 nm and for low concentration of the RE ions, five Stark components of the $4f^95d$ electronic configuration with maximum absorption at 66 800 cm^{-1} (149.7 nm), 69 300 cm^{-1} (144.3 nm), 70 323 cm^{-1} (142.2 nm), 72 337 cm^{-1} (138.2 nm), and 76 540 cm^{-1} (130.65 nm) were observed (Fig. 1). Similarly, in the spectral range from 153 to 170 nm, four Stark components of the $4f^95d$ electronic configuration with maximum absorption at 64 892 cm^{-1} (154.1 nm), 63 331 cm^{-1} (157.9 nm), 61 728 cm^{-1} (162 nm), and 59 523 cm^{-1} (168 nm) were observed as well. The bandgap of the crystal host was found to be at 80 700 cm^{-1} (123.9 nm). The cutoff wavelength of the LiF window placed in front of the hydrogen lamp and the solar-blind photomultiplier is at 110 nm. Therefore the absorption spectrum from 110 to 127 nm indicates only the position of the levels of the $4f^95d$ electronic configuration inside the conduction band and not the absolute value of the absorption coefficient. In this spectral range the value of the absorption coefficient is subject to large deviation from the average values because of the small signal-to-noise ratio.

B. Laser-Induced Fluorescence Spectrum

The laser-induced fluorescence (LIF) spectrum of the $LiLuF_4$:Ho^{3+} crystal under F_2 laser pumping in the spectral range from 157 to 300 nm is shown in Fig. 2. The
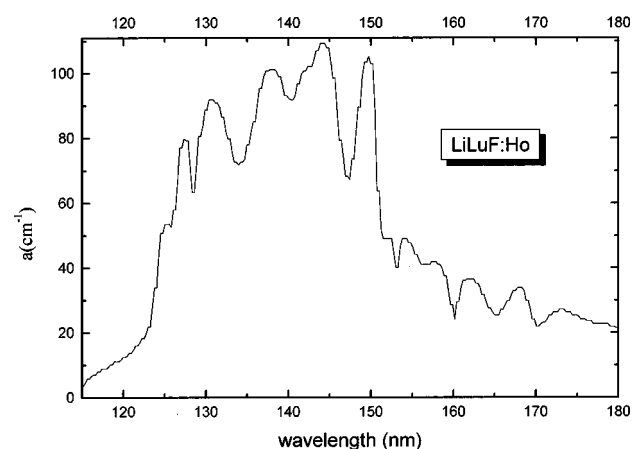

Fig. 1. Absorption spectrum of $LiLuF_4$:Ho^{3+} single crystal in the spectral range 120–180 nm. Nine transitions were observed between the $4f^{10}(^5I_8)$ ground level and the levels of the $4f^95d$ electronic configuration. The transitions in the spectral range 153–170 nm appear to be weaker than the transitions in the spectral range 125–150 nm. The 153–170 nm band was assigned to spin-forbidden transitions.[19] The low-energy limit of the bandgap of the crystal is estimated to be between 81 300 (123 nm) and 78 740 cm^{-1} (127 nm).
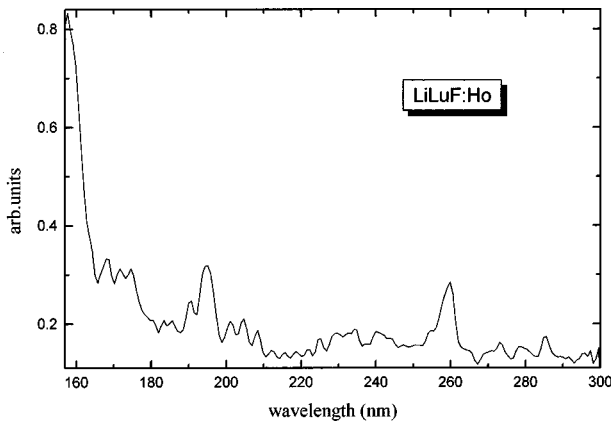
Fig. 2.   LIF spectrum of the LiLuF$_4$:Ho^{3+} single crystal, under laser pumping at 157.6 nm, in the spectral range 157–300 nm.

fluorescence peaks were assigned to the transitions between the levels of the $4f^9 5d$ electronic configuration and the levels of the $4f^{10}$ electronic configuration of the Ho^{3+} ion.   When the Ho^{3+} ion is excited from the $^5I_8$ ground level to a given level of the $4f^9 5d$ electronic configuration, it populates the levels of the $4f^{10}$ electronic configuration from the edge and the levels of the $4f^9 5d$ electronic configuration.[19,20]   The LIF spectra can be interpreted on the basis of spin-forbidden transitions, as in the case of LiYF$_4$:Er^{3+} crystal,[19] or phonon trapping of the modes of the crystal lattice inside the levels of the $4f^9 5d$ electronic configuration for the dipole-allowed transitions, as in the case[21] of LiYF$_4$:Nd^{3+}.

When a single optically active center absorbs one photon, competition starts between radiative and nonradiative transitions.   The nonradiative transitions are faster, and the ion will decay to the lower of the $4f^9 5d$ levels. However, in the case of electronic transitions from within the levels of the $4f^9 5d$ electronic configuration the emission spectrum could be interpreted on the basis of four different processes:

1.   The formation of optically active RE centers of different site symmetries, which might be present at high concentrations of the RE ions.
2.   Direct $4f^9 5d \rightarrow 4f^{10}$ emission from the levels of the $4f^9 5d$ electronic configuration.
3.   Emission from the levels of the $4f^9 5d$ electronic configuration due to the repopulation of these levels.
4.   Spin-forbidden transitions.

The formation of the optically active RE centers of different site symmetries should be excluded at least for low concentrations of Ho^{3+} ions, as is the case for the CaF$_2$ crystal.[15]   On the other hand, direct emission from the levels of the $4f^9 5d$ electronic configuration should take place only when (a) two successive electronic levels are well separated by the combined energy of few phonons and (b) when the energy difference is larger than $kT \approx 208$ cm^{-1} at $T = 300$ K.

However, according to Szczurek and Schlesinger,[15] there are 1878 electronic levels of the $4f^9 5d$ electronic configuration in the energy range from 80.0×10^3 to 60.0×10^3 cm^{-1}; therefore two successive electronic levels are separated by 11 wave numbers (assuming an even

distribution of the energy levels over the spectral range). Hence there is a small probability of direct transitions between the Stark components of the levels of the $4f^9 5d$ electronic configuration and the levels of the $4f^{10}$ electronic configuration.   Therefore the LIF spectrum for dipole-allowed transitions could be the correct interpretation, provided that the third process of the repopulation of the levels of the $4f^9 5d$ electronic configuration is taking place.   The repopulation occurs through phonon reabsorption and trapping within the levels of the $4f^9 5d$ electronic configuration.   These kind of processes have their origin in the strong ionic coupling between two different Ho^{3+} ions through multipole or exchange interactions, and they have been observed previously for other crystal samples as well.[21]   In fact, this effect was previously reported to take place for the excited states of ruby by Geschwind *et al.*[22]   They observed trapping of phonons, which are resonant with the E and $2A$ excited states. The phonon produced by the $2A \rightarrow E$ transitions at one ionic site is quickly trapped by another Cr^{3+} site in the E state, the latter being excited to the $2A$ state after the absorption of the phonon.   The repopulating process will cease when the trapped phonons escape from the active volume by frequency shifting through the interconfigurational transitions.   Phonon trapping is usually detected by observation of the fluorescent radiation from the excited levels to the ground state in experimental conditions similar to ours.   In the case of the trivalent Ho^{3+} ions, the $4f^9 5d \rightarrow 4f^{10}$ transitions originate from the levels of the $4f^9 5d$ electronic configuration at 63 451 cm^{-1} (157.6 nm), 62 207 cm^{-1} (160.7 nm), 60 532 cm^{-1} (165.2 nm), 58 714 cm^{-1} (170 nm) and 56 961 cm^{-1} (175.5 nm). Owing to the lack of any theoretical calculations for the levels of the $4f^9 5d$ electronic configuration above 59 000 cm^{-1},[23] it is difficult to make definite assignments for the transitions in the spectral range from 125 to 170 nm. The transitions from 153 to 170 nm were assigned to the interconfigurational spin-forbidden transitions.[19]   The energy position of the levels of the $4f^{10}$ electronic configuration is not known exactly for the LiLuF$_4$ crystal. However, because the electrons of the $4f^{10}$ electronic configuration are well screened by the electrons of different electronic configurations, the shift of the levels of the $4f^{10}$ electronic configuration in LiLuF$_4$, LaF$_3$, LaCl$_3$, and LiYF$_4$ crystals[24–27] and in liquid solutions[28] relative to one another should be small.   The $4f^9 5d \rightarrow 4f^{10}$ dipole-allowed transitions originate from the terms $^5H_7$, $^5I_8$ and $^5K_9$.[15]   These terms should split to the total number of 79 Stark components in the crystal field of LiLuF$_4$. From the absorption and the emission spectra of Figs. 1 and 2, the following assignments can be made (Fig. 3):

$$4f^9 5d \ (63\,451 \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5I_7) + h\nu \ (168.3 \ \text{nm}),$$

$$4f^9 5d \ (63\,451 \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5I_5) + h\nu \ (190.6 \ \text{nm}),$$

$$4f^9 5d \ (63\,451 \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5F_5) + h\nu \ (208.3 \ \text{nm}),$$

$$4f^9 5d \ (63\,451 \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5S_2) + h\nu \ (222.1 \ \text{nm}).$$

The lowest level of the $4f^9 5d$ electronic configuration is the $^7H_8$ one, and it should split into four doubly degenerate Stark components in the LiLuF$_4$ crystal field.   The four Stark components span the spectral region from 153 to 170 nm.   The transitions that originate from the

$4f^95d(^7H_8)$ electronic configuration at $62\,207$, $60\,532$, and $58\,814$ cm^{-1} are spin-forbidden:

$$4f^95d \ \ (62\,207 \ \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5I_8) + h\nu \ \ (160.7 \ \ \text{nm}),$$

$$4f^95d \ \ (62\,207 \ \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5I_7) + h\nu \ \ (174.8 \ \ \text{nm}),$$

$$4f^95d \ \ (62\,207 \ \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5I_6) + h\nu \ \ (185.4 \ \ \text{nm}),$$

$$4f^95d \ \ (62\,207 \ \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5I_5) + h\nu \ \ (194.8 \ \ \text{nm}),$$

$$4f^95d \ \ (62\,207 \ \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5F_5) + h\nu \ \ (212.4 \ \ \text{nm}),$$

$$4f^95d \ \ (62\,207 \ \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5S_2) + h\nu \ \ (228.8 \ \ \text{nm}),$$

$$4f^95d \ \ (60\,532 \ \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5I_8) + h\nu \ \ (162.9 \ \ \text{nm}),$$

$$4f^95d \ \ (60\,532 \ \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5I_7) + h\nu \ \ (180.4 \ \ \text{nm}),$$

$$4f^95d \ \ (60\,532 \ \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5I_6) + h\nu \ \ (201.2 \ \ \text{nm}),$$
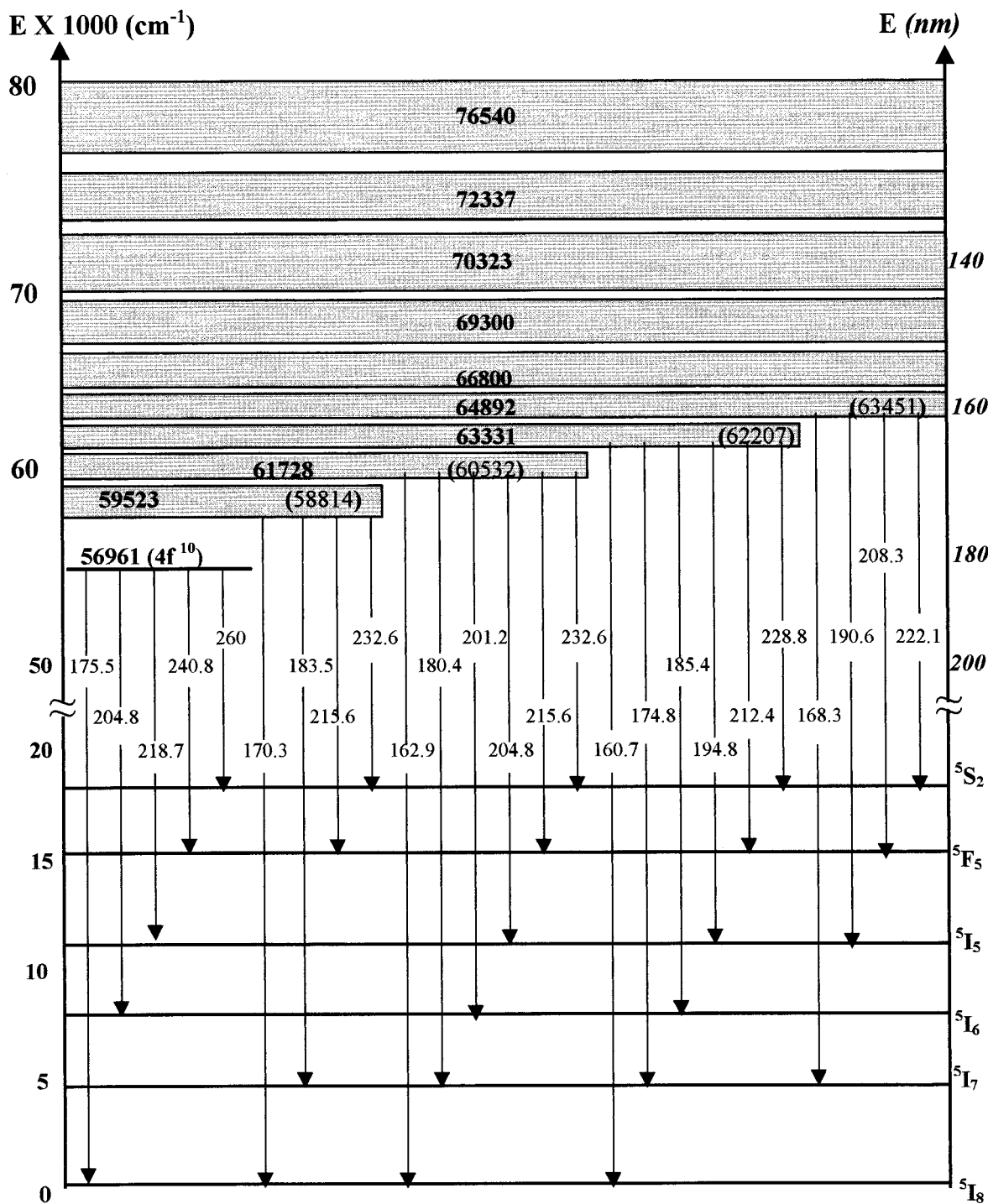

Fig. 3.   Energy diagram of the LiLuF$_4$:Ho^{3+} single crystal, where the various transitions of the LIF spectrum are shown.   The position of the levels of the $4f^95d$ electronic configuration is where maximum absorption is taking place.   The numbers inside the brackets indicate the energy position at which the Frank–Condon factors have their highest values.   The transitions are given in nanometers.

$$4f^9 5d \ (60\,532 \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5I_5) + h\nu \ (204.8 \ \text{nm}),$$

$$4f^9 5d \ (60\,532 \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5F_5) + h\nu \ (215.6 \ \text{nm}),$$

$$4f^9 5d \ (60\,532 \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5S_2) + h\nu \ (232.6 \ \text{nm}),$$

$$4f^9 5d \ (58\,814 \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5I_8) + h\nu \ (170.3 \ \text{nm}),$$

$$4f^9 5d \ (58\,814 \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5I_7) + h\nu \ (183.5 \ \text{nm}),$$

$$4f^9 5d \ (58\,814 \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5F_5) + h\nu \ (215.6 \ \text{nm}),$$

$$4f^9 5d \ (58\,814 \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5S_2) + h\nu \ (232.6 \ \text{nm}).$$

Similarly, the transitions that originate from the energy levels at $56\,691$ cm^{-1} can be assigned to the transitions between the levels of the $4f^{10}$ electronic configuration[18]:

$$4f^{10} \ (56\,961 \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5I_8) + h\nu \ (175.5 \ \text{nm}),$$

$$4f^{10} \ (56\,961 \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5I_6) + h\nu \ (204.8 \ \text{nm}),$$

$$4f^{10} \ (56\,961 \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5I_5) + h\nu \ (218.7 \ \text{nm}),$$

$$4f^{10} \ (56\,961 \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5F_5) + h\nu \ (240.8 \ \text{nm}),$$

$$4f^{10} \ (56\,961 \ \text{cm}^{-1}) \rightarrow 4f^{10}(^5S_2) + h\nu \ (260.0 \ \text{nm}).$$

4. CONCLUSIONS

From the laser induced fluorescence (LIF) and the absorption spectra of the Ho^{3+} ions in a $LiLuF_4$ single crystal it was found that the $4f^9 5d \rightarrow 4f^{10}$ dipole-allowed transitions originate from the edge and the levels of the $4f^9 5d$ electronic configuration. The $4f^9 5d \rightarrow 4f^{10}$ dipole-allowed transitions between the levels of the $4f^9 5d$ electronic configuration and between the levels of the $4f^{10}$ electronic configuration in the spectral region from 125 to 150 nm originate from the three terms $^5H_7$, $^5I_8$, and $^5K_9$. The transitions between the levels of the $4f^9 5d$ electronic configuration and between the levels of the $4f^{10}$ electronic configuration in the spectral region from 153 to 170 nm can be assigned to spin-forbidden transitions. The lowest level of the $4f^9 5d$ electronic configuration is the $^7H_8$ one, and it splits into four doubly degenerate Stark components in the $LiLuF_4$ crystal field. The LIF spectra for the dipole-allowed transitions can be explained, provided that phonon trapping of the lattice vibrations is taking place within the Stark components of the $4f^9 5d$ electronic configuration.

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